

## IS CO<sub>2</sub> DISPOSAL POSSIBLE?

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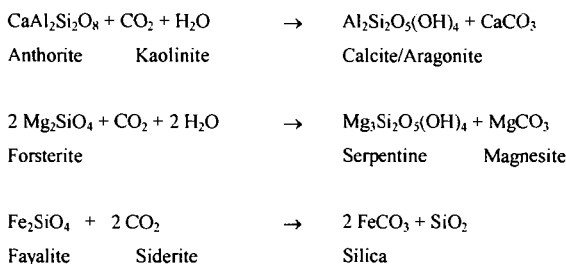
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### INTRODUCTION

Recently, Moore and Braswell<sup>1</sup> have reviewed the present state of knowledge of the carbon cycle. As they state: "the carbon cycle is still not adequately understood or quantified globally. Using averages for the 1980's, sources of atmospheric CO<sub>2</sub> exceed identified sinks by 1.8 - 1.2 PgC per year". It is interesting to examine their diagram of the global carbon cycle, and to note that there is essentially no attention given to processes deep in the earth's crust. One of the most interesting recent observations on the nature of the biosphere has been the discovery of thriving colonies of microorganisms at depth<sup>2</sup>. While workers on the alteration of seafloor basalts had suggested the actions of deep organisms, problems related to possible deep bio-corrosion of nuclear waste containers have stimulated more careful observations. Pedersen<sup>3</sup> has reviewed the present state of knowledge, and reported the present record of microorganisms at depths of 4.2 km below the surface, at temperatures up to 110°C.

### CO<sub>2</sub> AND THE THREAT OF GLOBAL WARMING

Emissions of greenhouse gases, including CO<sub>2</sub>, are on the rise. In developing countries, emissions are increasing the fastest and may soon equal those of developed countries. In countries like India and China, coal and other fossil fuels will continue to be a major source of energy for the next few decades. Thus emissions will continue to rise. Although programmes for reductions in greenhouse gas emissions are needed and encouraged, the inadequate actions by governments may soon make it necessary to develop alternative and more direct strategies to reduce the amount of greenhouse gases being emitted to the atmosphere. Currently, research on such strategies revolves primarily around three main ideas: disposal of CO<sub>2</sub> in the oceans, in deep aquifers, and in oil or gas reservoirs (IEA<sup>3</sup>). Another strategy involves the disposal of CO<sub>2</sub> in the form of carbonate minerals (Seifritz<sup>4</sup>; Dunsmore<sup>5</sup>; Lackner et al.<sup>6</sup>; Fyfe et al.<sup>7</sup>). In nature, such a process occurs on a global scale during the weathering of silicate minerals. Typical of such reactions are:



This natural sink of CO<sub>2</sub> accounts for nearly 80% of the sum of all carbon sinks. These reactions are exothermic. It has also been shown that these reactions can be catalyzed by microorganisms, such as cyanobacteria (Ferris et al.<sup>8</sup>; Tazaki et al.<sup>9</sup>). Thus, it is possible to enhance this 'natural' process to remove significant amounts of CO<sub>2</sub> from fossil fuel plants and from the atmosphere? Could CO<sub>2</sub> be pumped underground in suitable rock formations where microbial populations are plentiful? Can we enhance the growth of these microorganisms in situ to make the whole process feasible, a sort of bioremediation of the atmosphere? The exothermic nature of the reactions is an added bonus as geothermal energy could be used to partially 'fuel' the operation, make it more economically feasible, and produce useful warm water.

### CO<sub>2</sub> DISPOSAL

Seifritz<sup>4</sup> was one of the first to point out that the natural weathering of silicates resulting in carbonate mineral formation could potentially be enhanced as a way of permanently disposing of

CO<sub>2</sub>. Two problems were initially acknowledged: a sufficiently large source of Ca (and Mg-Fe) and the kinetics of the silicate-to-carbonate reaction. Dunsmore<sup>5</sup> suggested the evaporitic salts and brines of the Alberta Sedimentary Basin would provide an ample source of Ca and Mg, which could be transformed into carbonates. The advantage of using this basin is that it is in the heart of the fossil-fuel industry in Canada where existing infrastructures could potentially be modified for CO<sub>2</sub> transport and disposal. Lackner et al.<sup>6</sup> equally showed that common silicate minerals like olivine and plagioclase in rocks could also act as sources of Ca and Mg. As for the kinetics of reactions, microorganisms can enhance the rate of silicate weathering by producing organic acids (Hiebert and Bennett)<sup>10</sup> and catalyze carbonate precipitation by acting as nucleation sites for mineral growth (Ferris et al.<sup>7</sup>; Tazaki et al.<sup>9</sup>). Storage of CO<sub>2</sub> in carbonate minerals has also been briefly discussed in relation to aquifer disposal (IEA<sup>3</sup>; Bachu<sup>11</sup>) and ocean dumping (Harrison et al.<sup>12</sup>).

#### MICROBES, EXTREME ENVIRONMENTS, AND BIOMINERALIZATION

Microorganisms are able to survive in a wide variety of harsh environments, ranging from low to high temperatures, highly acidic to highly alkaline, saline, and dry conditions (Edwards<sup>13</sup>). The upper limit for thermophilic bacteria appears to be ~ 110°C, with some species showing optimum growth at temperatures as high as 105°C (Edwards<sup>13</sup>). However, many workers believe this upper limit could in fact be as high as 150°C, providing that the pressure is sufficiently high to increase the boiling point of water (Edwards<sup>13</sup>; Gold<sup>14</sup>). At deep sea hydrothermal vents, barothermophilic bacteria can also withstand immense pressures in addition to the elevated temperatures. Also bacteria can survive in very high concentrations of CO<sub>2</sub> at these vents (Childress et al.<sup>15</sup>).

Bacteria are not only ubiquitous at the Earth's surface and at deep-sea vents, but within the lithosphere as well. Bacterial populations have been found at over 4000 m deep in boreholes drilled into crystalline rocks in Sweden, in deep thermal groundwaters, in oil bearing sedimentary rocks, and over 1000 m deep in a basaltic aquifer (Pedersen<sup>2</sup>; Szewzyk et al.<sup>16</sup>; L'Haridon et al.<sup>17</sup>). In the latter case, the bacteria appear to derive their energy solely from hydrogen produced by geochemical reactions.

Microorganisms are known to influence carbonate mineral formation in a variety of environments from cold waters on lava plains in Iceland (Ferris et al.<sup>7</sup>; Tazaki et al.<sup>9</sup>) to hot springs in Kenya and New Zealand with water temperatures well above 90°C (Jones and Renault<sup>18</sup>). Biomineralization of Fe-Mn oxides and sulphides at high temperatures and pressures has also been reported from deep sea hydrothermal vents (Juniper and Tebo<sup>19</sup>). At these vents, microorganisms are also involved in the transformation and weathering of existing hydrothermal deposits.

#### WORK IN HAWAII AND ICELAND

In both Hawaii and Iceland, secondary carbonate minerals develop as weathering products from Ca and Mg silicates in fractures, cracks, pores, and in large sea caves of basaltic rock. Carbonate minerals identified by XRD include calcite (CaCO<sub>3</sub>) (see fig. 1) aragonite (CaCO<sub>3</sub>), magnesite (MgCO<sub>3</sub>), hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>(OH)<sub>2</sub> · 4H<sub>2</sub>O) and dolomite ((Ca,Mg)CO<sub>3</sub>). Other minerals such as clays and silica were also identified as weathering products.

Carbonate minerals were found in association with extensively fractured basaltic lava rocks in Iceland. These minerals occur in thin crusts on weathered basalt and their formation was shown to be mediated by microorganisms (Ferris et al.<sup>7</sup>). Calcite forming in a hot spring microbial mat in Iceland has also been shown to be influenced by microorganisms, in particular cyanobacteria (Tazaki et al.<sup>9</sup>).

In Hawaii, carbonate minerals appear to precipitate from meteoric waters trickling down the interior surfaces of large sea caves. The meteoric waters in the caves are most likely rich in organics as the exterior surface is densely vegetated. The carbonates occur in thin coatings (< ~5 mm) on the interior surface of the caves and in the near-surface pores, cracks and vesicles of the basalt 'host rock'. Our preliminary calculations show that a significant part of the missing carbon dioxide of the carbon cycle could be explained by such processes.

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#### Figures

Fig. 1. SEM image showing filamentous microorganisms on mineral surfaces of Hawaii basalt. The arrow points to  $\text{CaCO}_3$  crystals.



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